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Resonant inelastic x-ray scattering and UV–VUV luminescence at the Be 1s edge in BeO

A Kikas¹, T Käämbre¹, K Kooser^{1,2}, I Kuusik¹, V Kisand¹,
E Nõmmiste¹, M Kirm¹, E Feldbach¹, V Ivanov³, V Pustovarov³
and I Martinson^{4,5}

¹ Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

² Department of Physics and Astronomy, University of Turku, FIN-20014 Turku, Finland

³ Ural State Technical University–UPI, Mira street 19, Ekaterinburg, 620002, Russia

⁴ Department of Physics, Lund University, PO Box 118, SE-22100, Lund, Sweden

E-mail: Arvo.Kikas@ut.ee

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Abstract

We carried out a combined study of UV–VUV luminescence and resonant x-ray emission from BeO single crystals with incident photon energies in the vicinity of the Be 1s absorption edge. The x-ray emission spectra show that at the Be 1s photoabsorption edge the lattice relaxation processes in the excitation site take place already on the timescale of the radiative decay of the core excitation. Comparison of the x-ray emission and the luminescence spectra indicates that the maximum energy loss of the process of lattice relaxation during the decay of inner-shell holes is similar to the loss that occurs in the self-trapping process of valence excitons. The possible decay channels of core excitations have been discussed and the mechanism for the creation of 5.2 eV luminescence at the photoabsorption resonances has been suggested.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Insulating oxides have physical properties that make them useful in a wide range of applications. BeO has attracted attention due to its high thermal stability (melting temperature $T_m = 2550^\circ\text{C}$), wide transparency range extending from 120 to 7000 nm, high heat conductivity, mechanical hardness and radiation resistance. BeO crystallizes in the hexagonal wurtzite crystal structure, with the lattice point symmetry as low as C_{3v} . A consequence of the low symmetry is the strong anisotropy of the optical constants and luminescence properties.

A luminescence study using excitation in the vacuum ultraviolet (VUV) region (8–35 eV) [1] proposed that the excited states of excitons have a variety of configurations, which can be varied by choosing the excitation energy and the sample orientation, initially revealed in [2]. Two kinds of self-trapped excitons (STE) have been identified—excitons with axial localization of the hole component (STE1) and excitons

with radial localization of the hole component (STE2). It has been suggested [3], that the 6.7 eV emission corresponds to the decay of triplet STE1 and the 4.9 eV emission to the decay of triplet STE2. In this work we pay special attention to the peculiarities of the formation of the STE at Be 1s photoabsorption resonances.

However, the analysis of the soft x-ray excited luminescence spectra is a sophisticated task because the luminescence is a result of a sequence of the relaxation processes, which start from the creation of a core excitation (a core exciton or photoelectron and core hole). The inner-shell hole can decay radiatively, by emission of x-ray photon, or non-radiatively, when an Auger electron is emitted. As a result of this first relaxation step a photon or an Auger electron with energy slightly below the binding energy of the core electron is emitted. Alternatively, the incident photons have enough energy to ionize the valence shell, creating photoelectrons and valence holes. All the created electrons with energies above the ionization threshold lose energy mainly by electron–electron

⁵ Deceased.

scattering, creating secondary electrons and holes. When the energy of electrons is no longer sufficient for ionization, the consecutive energy loss occurs via scattering on phonons. During the terminal stage of the scattering sequence, the slow secondary electrons can become captured (i.e. become localized) by the valence holes, resulting in the formation of additional valence excitons. Due to the abundance of details and parameters in this sequence, no experiment follows all the steps of the relaxation. In this paper we look for analogous features in the emission spectra generated in the initial and the final stages of such a sequence—the resonant inelastic x-ray scattering (RIXS) and the STE radiative decay (luminescence) spectra.

The RIXS spectroscopy has proven useful for investigations of electronic processes, including the dynamics of core excitations. Unlike photoelectron spectroscopies RIXS is not affected by sample charging, thus it is particularly useful for crystalline bulk insulator studies for materials, like BeO, which are not easily obtained as thin films.

A few RIXS studies [4, 5] are closely related to the present work. Ma *et al* [4] observed the long energy loss tail to the elastic scattering peak, while in the absorption spectrum only a relatively sharp core exciton peak was observed. The authors suggested that strong vibronic coupling leads to a local lattice distortion, and to the corresponding shifts in the excited electronic state. The appearance of the energy loss wing in the *electronically* elastic part of the RIXS spectra indicates that such distortion occurs already during the lifetime of the inner-shell hole. More recently Harada *et al* [5] reported polarization dependence of such an energy loss tail at σ core excitations in graphite, and interpreted it as direct evidence of dynamic symmetry breaking upon core excitation. A similar phenomenon is typical of valence excitons in solids, where self-trapping of valence excitons occurs in the course of lattice relaxation, and the radiation emitted during the lattice relaxation process has been called ‘*hot luminescence*’ [6]. The term *hot luminescence* has even been introduced to describe the processes related to the appearance of the energy loss wing of the elastic peak in RIXS spectra [5, 7]. A similar energy loss wing has been observed in the RIXS spectra of LiNO_3 [8], where it was attributed to the dynamics of x-ray emission, accompanying the distortion of NO_3^- species. For BeO, we found in the RIXS spectra at the Be 1s edge an extraordinarily strong energy loss wing to the elastic peak, indicating overwhelming local reconfigurations in the vicinity of the absorption site during the lifetime of the core excitation [9].

Although quite different as regards the time-span, the similarities in the scope of the observed relaxational energy loss in the RIXS and luminescence spectra and in the possible pathways that may lead to these losses led us to the present comparative study. Such combination of the luminescence and the RIXS spectroscopies would provide insight into the understanding of the cascade of soft x-ray induced processes, which in the far end lead to the luminescence in the UV–VUV spectral region. BeO is a particularly suitable material for this study, because in the UV–VUV region both the STE and the free excitons have been observed [3, 10]. Additionally, the

resonant x-ray scattering elastic peak has acquired a dominant energy loss wing, which suggests that vigorous relaxation mechanisms become promptly activated.

2. Experimental details

A BeO single crystal of hexagonal prism shape with natural growth faces was used in this study. The shape of the sample allowed easy orientation with respect to the crystal axes. The crystallographic *c*-axis was parallel to the probed sample surface, and the crystal was oriented so that the *c*-axis was perpendicular to both the polarization and the detection directions.

The x-ray emission measurements were carried out on beamline I511-3 at MAX-Lab, Lund, Sweden [11]. The incidence angle was 10° (from the surface normal). The spectrometer (a Gammadata Scienta XES300) was at 90° to the incident beam propagation direction, and parallel to the polarization. The resolution of the beamline monochromator (a modified SX700 by Zeiss) was set to 0.1 eV. The resolution of the spectrometer on the end station was set to 0.2 eV. The size of the photon beam was approximately $30\ \mu\text{m} \times 30\ \mu\text{m}$. The base pressure of the system was 1×10^{-9} Torr. The x-ray emission measurements were performed at room temperature.

The luminescence experiments were performed at beamline BW3 at HASYLAB, DESY. The time-resolved luminescence spectra and luminescence excitation spectra as well as the decay kinetics of luminescence were recorded at temperatures of 10 and 295 K, as described in [12]. The resolution of the beamline monochromator (a Zeiss SX700) was 0.04 eV in the measurements of the excitation spectra. The size of the photon beam was approximately $200\ \mu\text{m} \times 100\ \mu\text{m}$. The luminescence spectra in the 2.5–8 eV region were measured by a 0.4 m vacuum monochromator (Seya–Namioka scheme) equipped with a microchannel plate-photomultiplier (MCP-PMT 1645, Hamamatsu).

The effective time-resolution of the detection system was approximately 250 ps (FWHM). Simultaneously with the time-integrated luminescence spectra, the spectra in the three time windows delayed relative to the excitation pulse were registered: the fast component with a delay time $\delta t_1 = 0.2$ ns, length of the time window $\Delta t_1 = 3.4$ ns; the first slow component with $\delta t_2 = 7.3$ ns, $\Delta t_2 = 28$ ns; and the second slow component with $\delta t_3 = 34$ ns, $\Delta t_3 = 118$ ns.

Cathodoluminescence of BeO crystals at 5 K was measured using the laboratory setup in Tartu. In these measurements the luminescence was detected by two spectrometers working in different spectral ranges: by a double grating VUV spectrometer equipped with a solar-blind PMT (Hamamatsu R6838) and by the spectrometer for UV/visible spectral range equipped with a Hamamatsu photon counting head H6240 as described in [13]. The electron gun has tunable electron energy in the range 1–30 keV, electron current 10–100 nA with a typical spot size $0.5\ \text{mm}^2$. In the present study the energy of electrons was tuned to 20 keV, which ensures their rather deep penetration depth to avoid disturbing surface effects.

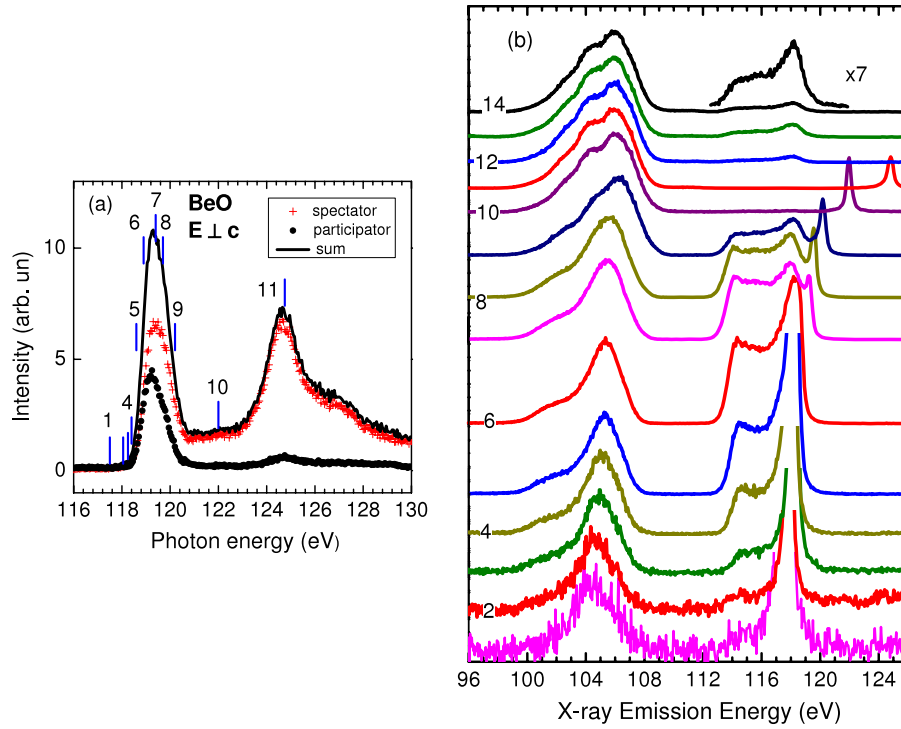


Figure 1. Panel (a) shows the Be 1s fluorescence yields of BeO. Crosses denote the photon yield of the ‘spectator’ (energy window 93–110 eV) and points the yield of the ‘participator’ (111–130 eV) transitions, measured using the XE spectrometer. The solid line denotes the total Be 1s fluorescence yield (the sum of the spectator and the participator yield spectra). The numbered tags denote the excitation energies of the x-ray emission spectra, presented in panel (b). Excitation energies for the off-resonant x-ray emission spectra 12, 13 and 14 are 131 eV, 133 eV and 145 eV, correspondingly.

3. The spectra

3.1. X-ray emission

Figure 1(a) displays the x-ray fluorescence yield spectra in the 111–130 eV (the ‘participator’ curve in the figure) and 93–110 eV (the ‘spectator’) detector energy windows. Two strong peaks are seen, at excitation energies 119.3 and 124.6 eV. These main peaks align well with the energy loss spectrum in the *non*-resonant inelastic x-ray scattering (NRIXS) study of BeO of [14]. This study also states that the NRIXS spectrum can only be reproduced by calculations if the core hole interaction with the excited electron is taken into account. Their calculations also gave a value of 0.74 eV for the energy distance from the exciton level to the bottom of the conduction band. A recent theoretical calculation of x-ray photoabsorption by Gao *et al* [15] has also confirmed that the presence of the core hole dramatically alters the distribution of spectral features and a sharp peak near the threshold is generated, when the core hole interaction is included into the calculation.

The development of the RIXS and several off-resonant x-ray emission spectra at the Be 1s edge of BeO is presented in figure 1(b). In the photon energy region 99–109 eV the emission band corresponding to the decay transition from VB to Be 1s level is seen. In the case of resonant excitation this emission band can be described as the ‘spectator’ emission, because the excited electron acts as a spectator during the core hole decay process. The spectator band emission is known in the case of off-resonant excitation as Be K α x-ray fluorescence

and it is commonly assumed that due to the dipole selection rules it reflects the density of p-states at the Be ion.

The high energy end of each spectrum is terminated by the sharp elastic scattering peak at incident photon energy. The elastic peak is seen to have an unusually strong energy loss wing at its low energy side, when the excitation is in the proximity of the photoabsorption resonance of 119.3 eV. We call the emission above the valence band top emission energies (the elastic peak and its low energy tail (LET)) the ‘participator’ emission (the excited electron participates in the decay event, i.e., the emission is due to the transition of the excited electron to the 1s level).

The low energy cut-off of LET of the elastic peak is at nearly constant photon energy, 113 eV, and it extends up to the elastic peak until the excitation energies reach the maximum of the photoabsorption peak at 119.3 eV. Thus its maximum width is about 6 eV. When the excitation energy is increased beyond the photoabsorption resonance energy, a valley appears between the LET and the elastic peak and the intensity of the LET quickly decreases. For excitations a few eV above the resonance the LET emission is no longer observable. We suggest that the LET band to the elastic peak appears due to the dynamic lattice distortion at the absorption site on the x-ray emission timescale, in line with the arguments in [5] and [8]. When the excitation energy is increased further and reaches values of approximately 130 eV, a satellite band, similar to the LET, appears again to the off-resonant x-ray emission spectra, although its intensity then is substantially weaker. This

energy, 130 eV, coincides well with the sum of band gap energy (10.6 eV) and photoabsorption maximum (119.3 eV) of BeO. Such a second threshold indicates that the band, which we observe as the LET in the case of resonant excitation, can be excited when the energy of valence photoelectron reaches the energy of core exciton.

The area of the sharp elastic scattering peak measures the transition without relaxation and the area of LET is a measure of the transition with the relaxation. At resonance, the small area of the sharp elastic peak in comparison to the LET shows that at photoabsorption resonance in most cases the relaxation has started (see curve 7 in figure 1(b)). However, we would like to mention here that the intensity ratio between LET of the elastic peak and the spectator emission is constant for fixed excitation energy, but the relative intensity of the sharp elastic peak changed strongly when we changed position at the crystal surface. This shows that the elastic scattering at the surface (reflection) gives its contribution to the sharp elastic scattering peak, but the intensities of the inelastic processes (the spectator and the LET participator band) reflect the fundamental properties of the bulk crystal. At the same time it should be kept in mind that the elastic peaks are weaker, but do not vanish elsewhere. The participator emission is, however, the only possible channel for the LET emission, because there are no other electrons available for this transition.

We now draw attention to the observation that the LET of the elastic peak has two maxima—at approximately 114.7 and 118.4 eV. Note that the lower energy maximum (114.7 eV) shifts slightly (less than 0.5 eV) to lower emission energies when the excitation energy exceeds the photoabsorption resonance. The higher energy maximum at 118.4 eV has an emission energy which is about 1 eV lower than the energy of photoabsorption resonance.

The participator transitions in solids can be treated as Franck–Condon transitions in systems of two potential curves, presented as a function of internuclear distance for molecules, or as a function of the configuration coordinate in solids. In the framework of this model the appearance of intense phonon losses demands sufficiently long lifetime for the system to relax to the new equilibrium position before the decay of the excited state, comparatively high phonon energies and strong shift of the excitonic state equilibrium position from the ground state equilibrium position, whereas most of the phonons are generated after the system decays back to the ground state. For BeO appearance of intense LET is made possible by a combination of the relatively long lifetime of the inner-shell hole (13 fs [16]) and the high energies of the lattice vibrations, which can extend up to 0.12 eV [17]. It is difficult to estimate the displacements, but we believe that observation of the self-trapped valence excitons confirms that sufficiently large displacements are possible. However, if the neighborhood of the excitation site becomes considerably altered during the core excited state lifetime, it becomes meaningful to introduce a third potential curve (see figure 2), which can be shifted in equilibrium coordinate and elasticity parameters. Earlier, Ma [4] has emphasized the similarity between the core exciton in carbon and the STE in alkali halides as they both relax to an off-center configuration upon generation. Soon after that it

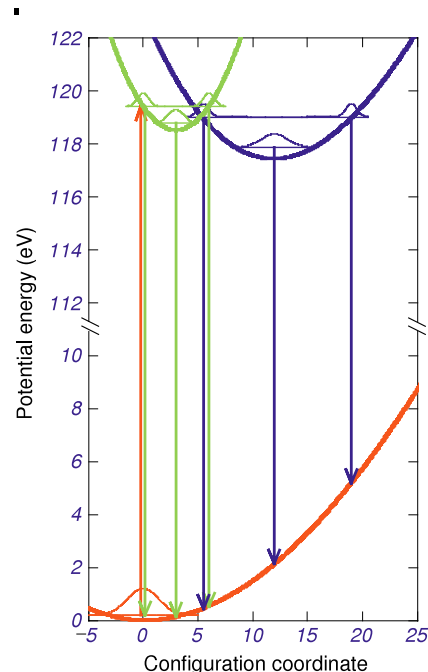


Figure 2. Schemes of possible transitions in the RIXS participator channel. Bottom curve: ground electronic state; left curve at top: unperturbed unoccupied state potential; right curve at top: excited state potential modified by local lattice relaxation. See text for further details.

has been shown for carbon that the reason for the appearance of a LET is the self-trapping of core exciton [18]. If we now suppose that even the Be 1s exciton in BeO becomes, similarly, self-trapped then the whole process should be described in the following manner—the photoabsorption makes the transition of an electron from the ground state to the intermediate state (green curve at top left in figure 2); however lattice distortion will change the potential curve so that the decay already occurs from a relaxed state (top right blue curve in figure 2). The relaxation processes also cause the system to ‘slide down’ along the excited state potential curves, and if the relaxation rate is comparable to that of the decay processes, this leads to the emission from different states on the potential curves of the excited state. If the relaxation is very fast, the system promptly relaxes to the minimum of the excited state curve, and only the transition from the minimum should be seen (shown as the middle blue arrow). The observed wide LET shows that the transitions are from a progression of intermediate states in different stages of relaxation, which makes the whole process similar to the hot luminescence in the optical region. It is interesting to note that in the excitation spectra of the spectator band the two peaks are of almost equal intensity (similarly to the energy loss spectrum of NRIXS in BeO [14] and calculated x-ray absorption spectra [15]), but in the participator band excitation spectrum the 124 eV maximum is almost absent, indicating the absence of core excitons at this excitation energy. Even the first excitation resonance can be divided into two energy regions: below the participator peak maximum (at 119.2 eV) a strong LET appears in RIXS to the elastic peak, indicating strong localization of the excited electron.

Above this energy, the participator band loses its intensity faster than the spectator band, and the spectator channel (with maximum at 119.4 eV) starts to dominate. The weakening of the participator band suggests increasing delocalization probability for the excited electron. As stated above, the appearance of the broad participator emission indicates strong localization of the excited electron. Therefore we consider the participator excitation spectrum as predominantly the core exciton excitation curve.

Note that increasing the excitation energy in the absorption resonance region makes the spectator band maximum shift to higher photon energies, which reflects the RIXS energy conservation. In the case of resonant excitation the maximum of this band is at about 1 eV lower photon energy as compared to the off-resonant excitations. A similar shift has been observed earlier for spectator transitions in many cases. It reflects the phenomenon that the ionization energy for the spectator electron is usually larger in the core excited state than in the valence excited state ([8] and references therein). The spectator shows additional structures at off-resonant excitation (spectra 12–14 in figure 1(b)).

Above we described the participator emission as strongly influenced by the lattice relaxation. We speculate that even the Be 1s spectator emission should be sensitive to the relaxations. This is supported by a recent study on adsorbed ethylene [19], where it is shown by the comparison of calculated and measured spectra. Similarly to the case of radiative participator decay, this may lead to the widening of the corresponding VB spectra in comparison with the calculated VB density of states [20, 21]. Considering this, we may interpret the changes in the spectator spectrum as indications of analogous energy loss features. However, due to the overlap of different final states these effects are not as clearly distinguished as in the case of the participator band.

3.2. Luminescence

The lower panel of figure 3 shows the cathodoluminescence spectra of BeO at 5 K, excited by 20 keV electrons. This is a good starting point for the analysis of the luminescence spectra of soft x-ray excitation because it gives the general view and the positions of the luminescence bands, which can be assumed to appear at the selective excitation with narrow band radiation.

The faint sharp peak at 10.3 eV is due to the decay of free excitons [10]. The radiation in the 8–9 eV range is emitted during ongoing relaxation, i.e., this is hot luminescence of valence excitons. The two relatively broad luminescence bands peaked at 4.9 and at 6.7 eV are induced by the radiative decay of two different STEs, which are distinguished on the basis of their valence hole configuration within the crystal unit cell [3].

The building blocks of a BeO crystal are distorted tetrahedra (C_{3v} symmetry) with the beryllium ion at center position and the O ions at vertices: the axial position (more distant from the Be cation) and three equivalent radial positions can be identified for each local tetrahedron. It has been suggested [3] that the 6.7 eV emission corresponds to the STE with the valence hole localized on the axial anions (STE1) and the 4.9 eV emission to the excitons with the hole nucleus

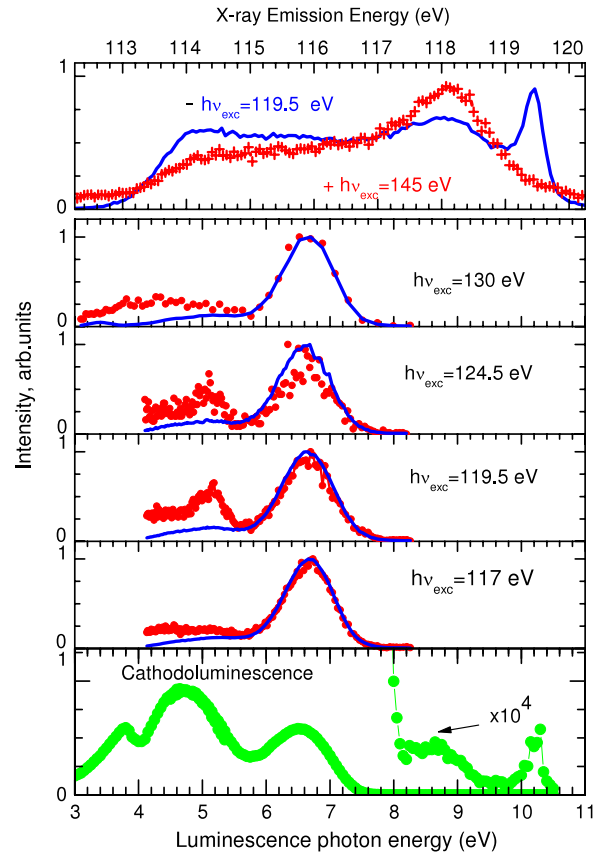


Figure 3. Lower panel: cathodoluminescence spectra of BeO crystal at $T = 5$ K, excited by 20 keV electrons. Middle panels: x-ray excited luminescence spectra of BeO crystals for $T = 8$ K. Dots denote spectra measured in the fast time window (measured 0.2–3.6 ns after the excitation). Lines denote the time-integrated luminescence spectra. Upper panel: the x-ray emission spectra. The spectra are shifted so that at the resonant excitation the elastic peak coincides with the luminescence of free excitons at 10.3 eV.

localized on the radial anions (STE2). The 6.7 eV emission originates mainly from the STEs, which arise as result of self-trapping of free excitons, but the 4.9 eV emission originates mainly from excitons which are created by the recapture of a slow photoelectron to a self-trapped hole [3]. Also it has been suggested [3] that the 6.7 eV emission corresponds to the decay of triplet STE1 and the 4.9 eV emission decay of triplet STE2.

In the x-ray excited luminescence spectra, presented in the middle panels of figure 3, the strong STE peak dominates at 6.7 eV for all excitation energies. It has a shoulder, which extends from 4 to 5.5 eV. For the spectra which were measured in the ‘fast’ time window (0.2–3.6 ns after the excitation) this shoulder is strongly enhanced at resonant excitation (at 119.5 and 124.5 eV), resulting in a band with a maximum at 5.2 eV. It has been suggested that this band originates from decay of the singlet STE2 states [22]. Note that the spectra measured in slower time windows practically coincide with the integral spectra [22] and thus they are not presented here.

Earlier we mentioned that decay of core excitations and valence excitons can be described by using a similar scheme of potential curves (see figure 2), consequently there should be also some similarities in decay patterns. To see them, we

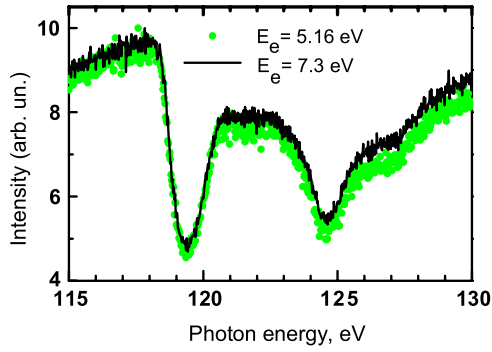


Figure 4. Luminescence excitation spectra of 5.2 eV band (measured at 5.16 eV) and 6.7 eV band (measured at 7.3 eV) emission in BeO crystals at $T = 8$ K.

present in figure 3 also the x-ray emission spectra. They are shifted so that the elastic peak at resonant excitation coincides with the emission of free excitons in luminescence spectra, i.e. it is compared with luminescence in energy loss scale. Note that the off-resonant x-ray emission spectrum in figure 3 is not aligned to zero loss because this spectrum reflects the decay of core excitations, created by the photoelectrons, resulting in valence photoabsorption (see section 3.1). Thus the selected alignment compares the energy losses during the different creation–decay sequences. From this comparison it can be seen that in the x-ray fluorescence all values of losses up to 6 eV are possible, but in the x-ray excited luminescence the 6.7 eV emission dominates, corresponding to the loss of 3.9 eV. The energy loss for the relaxation is stronger in the case of x-ray emission than in the case of luminescence. Probably this is due to the circumstance that the core hole is more localized than the valence hole, and thus has a stronger influence on the final state electron. However, it is clearly seen that losses up to 6 eV are possible in luminescence spectra, showing that the maximum loss energy is similar in both processes.

Figure 4 shows the excitation spectra of the 6.7 eV band (the actual detector energy was set to 7.3 eV to minimize the contribution from the energy bands of lower emission energy) and the 5.2 eV bands. As usual in the soft x-ray region, the excitation spectra show the minima at 119.3 and 124.6 eV, where the photoabsorption has maxima. This reflects the circumstance that with the increase of the photoabsorption the mean absorption depth decreases. Correspondingly there is higher probability to lose the non-thermalized charge carriers through the surface, and thus the probability for luminescence decreases. The excitation spectra of both luminescence bands are very similar. It is because these spectra are time-integrated spectra, but the 5.2 eV band appears clearly in the fast time window, and probably its intensity is too small to change the time-integrated spectra. Note that at the 124.4 eV excitation energy the luminescence intensity has similar value to at 119 eV excitation energy. This leads us to the conclusion that these spectra may be connected with the excitation of spectator x-ray emission, where the intensities of photoabsorption peaks are also similar, contrary to the participator emission, where the high energy maximum is absent.

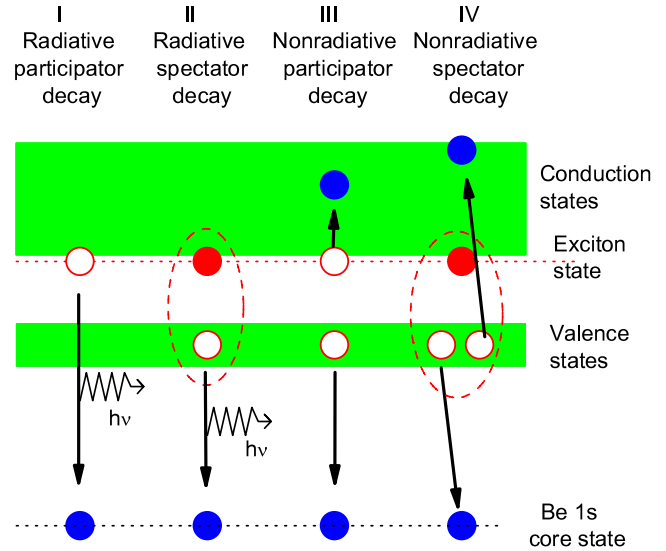


Figure 5. Scheme of decay channels of Be 1s core exciton state.

4. Discussion

In this section we will look for connections between the decay of core excitation (exciton or hole) and luminescence processes. At 119 eV excitation energy the excited electron is moved to the excitonic state near the bottom of the conduction band, and the core-hole–electron bound states, core excitons, are created. There are at least four possible decay channels of the core exciton state (see figure 5): (I) radiative participator, (II) radiative spectator decay, (III) non-radiative participator (Auger) and (IV) non-radiative spectator (Auger) decays.

Process (I), the radiative participator decay is the transition where the excited electron fills the core hole. Above we saw that during this transition the lattice relaxation occurs, causing the appearance of the long (about 6 eV) LET to the elastic peak. Thus the mean energy of the resulting photon can be written as $\hbar\omega_I = E_i - E_{ex} - E_{r1}$, where E_i and E_{ex} denote the binding energy of electron in inner level and excitonic level, correspondingly, and E_{r1} denotes the energy loss due to relaxation during this process. The whole process of radiative participator decay is similar to hot luminescence, which is emitted during the creation of valence STEs in alkali halides [6]. This process results in relaxed lattice and x-ray photon.

Process II, the radiative spectator decay, is a process where the core hole is filled by a valence electron. It was speculated above that the lattice relaxation should influence also this process. Then the energy of the photon emitted during this process can be written as $\hbar\omega_{II} = E_i - E_v - E_{r2}$, where E_v denotes the binding energy of the electron in the valence band and E_{r2} denotes the energy loss to lattice relaxation during the radiative spectator decay. The final products of this decay channel of core exciton are valence hole and excited electron—i.e., valence exciton. When the core exciton is self-trapped, i.e., the lattice relaxation has taken place during the timescale of the decay of the core exciton, this lattice relaxation can promote also the anion excitation self-trapping.

Besides the radiative decay processes also the non-radiative decay processes should be taken into account. Also in that case we will assume that the lattice relaxation has occurred before the decay, i.e., core exciton is self-trapped. Non-radiative participator decay (process III in figure 5) is an Auger process, where the electron from the valence band fills the core hole and the electron from the excitonic level is removed from the atom. The corresponding participator Auger electron has energy $E_{\text{pA}} = E_i - E_{\text{ex}} - E_v - E_{\text{r3}} = \hbar\omega_{\text{exc}} - E_v - E_{\text{r3}}$. Note that if we do not take into account relaxation ($E_{\text{r3}} = 0$), then the energy of this electron is equal to the energy of the photoelectron, arising in ionization of the valence band. The final state of the ion is a state with valence hole, and as the core hole is self-trapped (i.e., local lattice distortion has occurred at the core hole site), we suggest that the created valence hole is also self-trapped.

Process IV, non-radiative spectator decay, is a process where the inner-shell hole is filled by the valence electron, and another valence electron is removed from the atom. This process gives us an ion with two valence holes, excited electron and Auger electron with energy $E_{\text{sA}} = E_i - 2E_v - E_{\text{r4}}$. In the soft x-ray region the Auger process is a dominating process of decay of core hole, we believe that it also is in this case. Often the products of non-radiative decay of core excitations can be studied by resonant Auger spectroscopy. Unfortunately we cannot apply it for BeO, because for insulating monocrystals the measurement of resonant Auger spectra is practically impossible due to charging effects. Also, to our knowledge there are no stoichiometric thin films of BeO available. It is difficult to estimate the strength of the Auger processes. The atomic approaches cannot be used in this case, because the initial state is localized at the Be atom, but the final valence states are originating mainly from oxygen, and thus probably the overlapping between the initial and final states is small. We believe that this decreases the probability of non-radiative decay and increases the probability of radiative decay, making the lifetime of the inner-shell hole longer than in atomic beryllium, where it is 13 fs [16]. Thus there exists similarity with cross-luminescence, where Auger decay is energetically forbidden, but here it is suppressed due to weak overlap of wavefunctions. Probably this inhibition of non-radiative transitions is a reason why in BeO the radiative decay (x-ray emission) is quite strong and also the lattice relaxation is well observable.

To account for the possible initial states of the luminescence, we should also keep in mind that both the spectator and the participator radiative decay produce soft x-ray photons (with energy around 105 or 117 eV, correspondingly). Some of them are absorbed in the crystal, ionizing the valence band and creating new electron–hole pairs or valence excitons. This is similar to the processes which take place in excitation with photons with energy below threshold (for example, at 117 eV). Consequently, there will appear about ten electron–valence hole pairs or valence excitons. Some of the electrons are recaptured by holes, creating valence excitons.

Note that process (I), the radiative participator decay, produces a photon with energy (almost) equal to that of the

incident photons, and process (III), non-radiative participator decay, gives the same final state as valence ionization. Thus these processes cannot be responsible for changes in luminescence at photoabsorption resonances. Process (II), radiative spectator decay, may give us directly the valence exciton, which is one way to self-trapping, and process (IV), non-radiative spectator decay, gives us a trion, the bound state of two holes and an electron. The latter two processes appear to be the plausible candidates for causing changes in luminescence spectra and kinetics at core exciton resonant excitation. Note that all these processes will leave behind either a photon or an electron with an energy of about 100 eV, able to create about ten electron–hole pairs, similarly to the off-resonant excitation process. Thus there will be about ten ‘usual’ electron–hole pairs, and less than one ‘special’.

If the energy of incident photons $\hbar\omega_{\text{ex}}$ is higher than the photoionization threshold, the participator processes are not possible, because the excited electron is delocalized. Then the core hole with binding energy E_i and a slow photoelectron with energy $E_e = \hbar\omega_{\text{ex}} - E_i$ are created. The core hole can decay by the non-resonant radiative or non-radiative (Auger) process. In the case of radiative decay the final state will consist of a valence hole with energy E_v and an x-ray photon with energy $\hbar\omega_{\text{emis}} = E_i - E_v$ (and a slow photoelectron). At low photoelectron energies the photoelectron may rapidly lose energy by phonon scattering [23] and can be recaptured to a core hole site and in that way give rise to additional core excitons. After non-radiative Auger decay there will be final state with two valence holes and an Auger electron with energy $E_A = E_i - 2E_v - E_{\text{rA}}$, and a slow photoelectron. When the photoelectron energy is small, it is also possible that the two-hole state captures a photoelectron during the Auger process. This is known as post-collision interaction induced recapture (PCI) [24, 25]. In solids the phonon scattering will raise the probability of similar a recapture process in comparison with atoms [26].

To summarize: there are at least three possibilities for creation of valence excitons—(a) by the inelastic collisions during the electron–electron scattering and recapture of slow electrons by holes during the phonon scattering stage, which should be taken into account in the case of all four core hole decay scenarios, described in the previous section; (b) by the radiative spectator decay of the core exciton, as a direct excitation in the course of RIXS, with energy loss characteristic of a valence excitation (process II); and (c) by the decay of the two hole–electron state, resulting from the Auger spectator decay (process IV) or PCI induced recapture.

At all excitation energies the pathway (a) is likely the dominating process, because most of the energy is dissipated in the crystal in the course of the process of the inelastic electron scattering in the crystal. This results in electron–hole pairs, which by recombination create mainly the STEs, emitting 4.9 eV photons, similarly to the case of cathodoluminescence [10]. Observation of the enhancement of 5.2 eV luminescence at resonant excitation shows that additional channels are dominating at resonances. These are probably the channels (b) and (c).

However, the 5.2 eV luminescence is enhanced at both the 119.3 and the 124 eV resonances. Therefore the radiative

spectator decay (process II) cannot be responsible for it, because it is not available at the 124 eV resonance since the excited electron is not localized. We suggest that the process (IV), which produces a trion state, is responsible for this 5.2 eV luminescence. At 124 eV excitation energy, which is clearly above the photoionization threshold, the trions can be created by the recapture of a slow photoelectron to an Auger decay site with two valence holes, a phenomenon which has earlier been observed in NaF [25].

Above we have seen that when the excitation energies coincide with the photoabsorption maxima at 119.5 and 124.5 eV, there appears a fast (with lifetime of about 0.7 ns) decay component of the UV-luminescence of BeO crystals with characteristic energy of 5.2 eV. As this component appears at both photoabsorption resonances, and we saw above that for both resonances the trion creation is possible, we suggest that trions play an important role in the appearance of the fast 5.2 eV band. A trion can recapture a thermalized electron, which then can recombine with one of the holes of the trion, resulting in a two hole–two electron state. This state can decay into two (self-trapped) valence excitons, or into a photon and a self-trapped valence exciton. The valence excitons produced in such a way may have untypical localization of the hole component, and therefore their radiative decay may lead to a luminescence emission band at 5.2 eV (shifted 0.4 eV from the typical 4.9 eV emission energy of the self-trapped valence excitons).

To summarize, we therefore suggest that the core excited states that display large energy loss to dynamic lattice distortions are not straightforwardly seen to proceed through decay transitions into the valence excited states, which display similar energy loss due to self-trapping. It rather would seem that the excitations, whether core or valence, would induce local lattice relaxation which is of similar magnitude.

5. Conclusions

We present the results of a comparative study of x-ray emission and luminescence emission on electronic and vibrational processes in BeO by using for excitation the photons in the vicinity of the Be 1s absorption edge. The x-ray emission spectra show that at the Be 1s photoabsorption edge the lattice relaxation processes in the excitation site take place already on the timescale of the radiative decay of the core excitation. The analysis of possible decay channels of core excitations showed that the creation of bound states of two holes and excited electrons (trions) plays an important role in the appearance of the new fast luminescence band at 5.2 eV at photoabsorption resonances. Comparison of the x-ray emission and the luminescence spectra shows that the maximum value of energy loss to the lattice relaxation during the decay of inner-shell holes is similar to the loss due to the self-trapping of valence excitons, even if the significant features in the luminescence spectra do not straightforwardly appear to relate to the final state of the core exciton decay.

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